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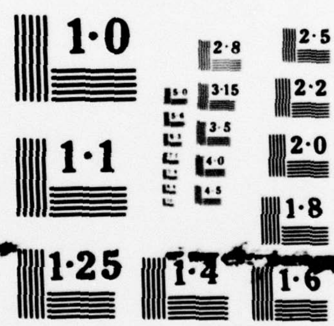


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# INVESTIGATION OF ELECTRON ATTACHMENT IN POLYATOMIC MOLECULES

Annual Technical Progress Report
1 April 1978 - 31 March 1979

Contract Number: F49620-77-C-0071
Principal Investigator: Dr. J. T. Dowell

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May 31, 1979





IRT Corporation

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CONTENTS

# 1. RESEARCH PROGRAM

The present research is concerned with the investigation of low energy, two-body attachment processes in molecules with particular emphasis on labile species and on temperature dependences of attachment cross sections. Specific molecules to be studied in the program include those of high interest for advancement of theoretical understanding of resonant electron-molecule scattering and for practical application to plasma engineering. Some background information and a description of techniques for attachment measurements are contained in our original proposal (IRT No. 4876-246, dated 25 August 1976) and our last technical progress report (IRT No. 8164-001, dated April 28, 1978), so that only a brief summary will be presented here.

Ideally, studies of two-body electron attachment should include measurement of the following:

(1) Variation of attachment cross sections with electron energy, and with gas temperature.

(2) Product negative ion kinetic energies as functions of incident electron energy.

(3) Energies and characteristics of resonances in total scattering.

(4) Attachment rates as functions of temperature.

Rate measurements are not particularly useful for basic studies, but are usually necessary for engineering applications. If the attachment cross sections are measured with sufficiently good electron energy resolution and the measurements extend down to the lowest electron energy at which attachment occurs, then rates may be calculated from the cross section data and experiments to measure them are unnecessary. The cross section for attachment at a particular electron energy usually depends very strongly on the excitation state of the target molecules, so that measurements of the temperature dependences of the cross sections, where possible, are quite important. Information on the energetics (e.g., bond energies and electron affinities) of the molecules studied is obtained from the kinetic energy measurements, and investigation of the scattering resonances yields insight into the compound states which so strongly influence all scattering channels (including attachment).

The primary experimental technique employed in the present program is that of crossed molecular and electron beams. A molecular beam of the species of interest is crossed with a monoenergetic electron beam of variable energy, and negative ions formed by two-body attachment in the intersection region are extracted, mass analyzed, and detected. The gas temperature dependence of the cross sections is obtained by variation of the molecular beam source temperature.

## 2. PROGRESS

Progress prior to the beginning of the present contract period was summarized in our last technical progress report. Briefly, exploratory experiments on attachment in $H_2WO_4$ and in $WO_3$ polymers were performed, and a high-resolution electron monochromator was constructed and tested in the molecular beam apparatus. Good energy resolution was obtained and design expectations were exceeded.

In the initial part of the present contract period, instrumentation was installed for the quadrupole mass filter and the ion counting system. After careful attention to shielding and grounding, the mass filter operated to greater than mass 1000 without significant rf pickup in the detection electronics. The ion detection system can now be operated with synchronous detection or with asynchronous pulse counting. The synchronous pulse counting and data logging systems have yet to be installed.

For a check on performance of the monochromator-quadrupole system, some aspects of electron attachment in $SF_6$ were investigated. Studies of $SF_6$ attachment have been performed by several workers, so that many characteristics of the process can be considered to be well known. The cross section for $SF_6^-$ formation is thought to be essentially a delta function at zero electron energy, so that the electron energy dependence of the measured cross section is simply the energy distribution of the electron beam. Attachment in $SF_6$ thus serves as a very useful diagnostic tool for high resolution electron beam systems.

Energy resolution deduced from the $SF_6$ studies was 0.03-0.05 eV FWHM at greater than 1 x $10^{-8}$A beam current. The temperature dependence of attachment in $SF_6$ was qualitatively investigated, and agreement was found with unpublished work of Chantry. Briefly, the $SF_6^-$ cross section rapidly decreases with increasing molecular beam source temperature, whereas the $SF_5^-$ cross section (which is also a delta function at zero energy) increases with temperature. The two are equal at about 600K. The broad $SF_5^-$ peak at about 0.4 eV is nearly independent of temperature.

During our discussions of $SF_6$ with Dr. P. J. Chantry, it was learned that he is publishing a comprehensive paper on attachment in that gas. We hope to soon receive a preprint of that paper in order to judge whether or not some of our results are publishable. In a sense, Chantry's experiments and ours may be complementary, since our apparatus performs much better than his near zero electron energy and has better energy resolution, whereas his is somewhat more convenient for investigating attachment at higher energies.

Since the $SF_6$ studies showed the apparatus to be functioning properly down to zero electron energy, measurements were begun on $WO_3$ and its polymers. Initially, a tungsten foil oven beam source was used, as in the exploratory experiments. Oxygen was flowed through the oven, so that $WO_3$ vapor was formed for temperatures above 1400K. [The vapor is composed of $(WO_3)_n$, n = 1, 2, 3, and other polymers, with $(WO_3)_3$ being the most abundant species for the temperature range used.] Fairly good $WO_3^-$ signals were observed, but the beam density varied so rapidly with time that measurements of the energy dependence of the cross section were not possible. Oven lifetime was about two hours. Several oven configurations were tried in attempts to achieve a stable beam and long oven life. Finally, an oven was constructed of iridium, sapphire, and tungsten that yielded a reasonably steady beam of tungsten oxides. Beam intensities were not strong, and became weaker with time, but the oven was not subject to failure.

Some data on attachment in $(WO_3)_n$ obtained with the new oven is shown in Fig. 1. Data for $SF_6^-$ taken just prior to the $WO_3^-$ run is exhibited for comparison. The electron energy resolution was better than 0.04 eV FWHM. The small peak at 0.04-0.05 eV in the $WO_3^-$ curve may be real since it has appeared in all data taken so far. If the attachment process is indeed $e^- + (WO_3)_3 \rightarrow WO_3^- + (WO_3)_2$,

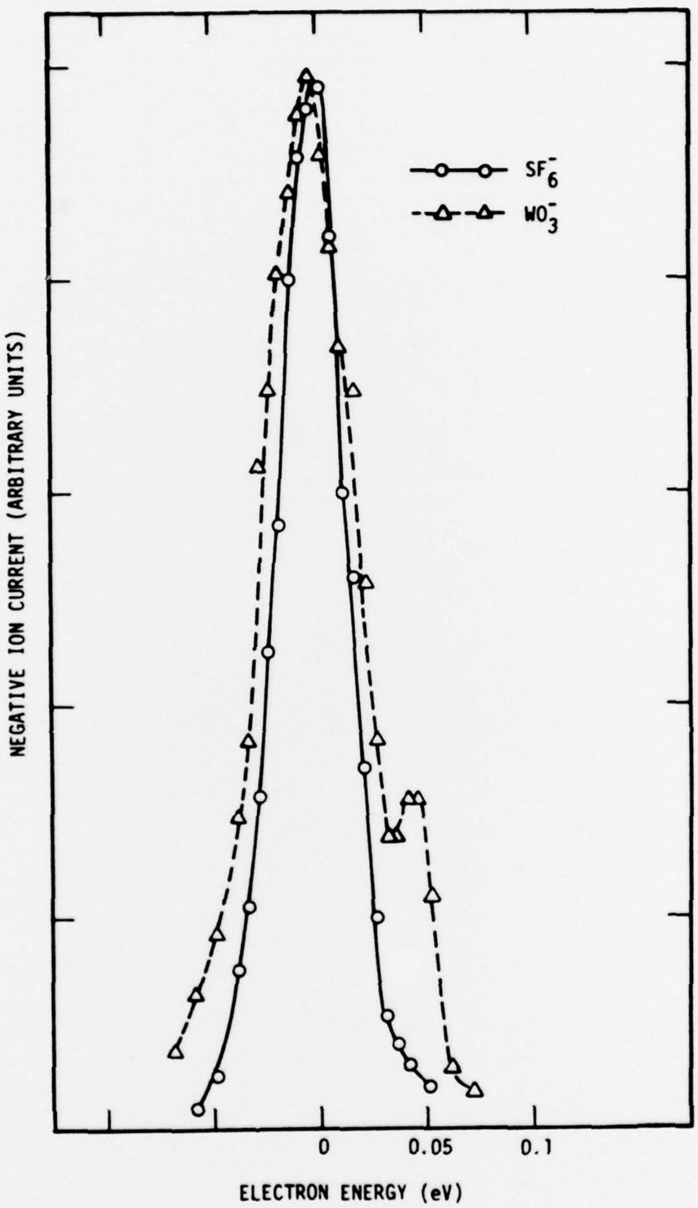


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Figure 1. Relative negative ion current for $WO_3^-$ and $SF_6^-$ vs electron energy. The $WO_3^-$ curve is normalized to that of $SF_6^-$ at the peak. Beam source temperature was 300K for $SF_6$ and 1740K for $(WO_3)_n$.

as suggested by the exploratory experiments, then this small peak may represent vibrational excitation of the dimer fragment. [The JANAF Tables show a vibrational mode of $(WO_3)_2$ at about 0.04 eV.] Formation of $(WO_3)_2^-$ appears to have an energy dependence similar to that of $WO_3^-$.

A quantitative measure of the absolute attachment cross section has not yet been obtained. The negative ion currents are greater than the positive ion currents (at the appropriate energies), so that the $WO_3^-$ cross section is probably greater than $2 \times 10^{-15}$ $cm^2$.

Very recently, results of some plasma quench investigations with tungsten oxide have been reported (J. M. Madson, 17th Aerospace Sciences Meeting, New Orleans, January, 1979—to be published in J. AIAA). In that work it is shown that the major attachment process in tungsten is $e^- + W_3O_9 \rightarrow WO_3^- + W_2O_6$, with some evidence of the reaction $e^- + W_3O_9 \rightarrow W_2O_6^- + WO_3$, in agreement with our conclusions. No energy dependence of the attachment could be obtained in the plasma experiments. Some of the tungsten oxide vapor pressure data contained in that report may allow our $WO_3^-$ results to be put on an absolute basis with a few further measurements. It is intended that the present tungsten oxide work be published soon.

An investigation of attachment in $MoF_6$ and $WF_6$ was begun during the present contract period. Results to date are summarized in a separate topical report. Much of the attachment observed was due to impurities, $MoOF_4$ and $WOF_4$. Energy dependences of the cross sections for $MoOF_4^-$ and $MF_6^-$ were determined and magnitudes of the cross sections relative to $SF_6$ were measured. This work should be a useful contribution to the study of zero-energy attachment processes.

Since the hexafluoride studies are taking longer than anticipated, experiments on the alkali halides have not yet been started. Those investigations will be initiated when the hexafluoride and tungsten oxide work has been completed and submitted for publication.

## 3. PROFESSIONAL PERSONNEL ASSOCIATED WITH PROGRAM

Personnel working directly on the project include Dr. J. T. Dowell (Principal Investigator) and Mr. J. A. Rutherford. Dr. D. A. Vroom, Dr. S. M. Trujillo, and Mr. R. L. Palmer have also contributed to the program through useful interactions. Informative discussions with Dr. K. Westberg (Aerospace Corporation), Prof. P. D. Burrow (University of Nebraska), and Dr. P. J. Chantry (Westinghouse Research Laboratories) are gratefully acknowledged.

## 4. PROFESSIONAL INTERACTIONS

The principal investigator attended the 31st Annual Gaseous Electronics Conference (17-20 October 1978), Buffalo, N.Y. [No paper was presented.]